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Upgrading fast pyrolysis liquids: Blends of biodiesel and pyrolysis oil

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HIGHLIGHTS

- ▶ Homogenous blends of bio-oil/biodiesel were prepared with the use of alcohol.
- ▶ The blends were subject to visual and analytical tests, including adapting the empirical stability test used for bio-oil.
- ▶ Three phase charts were built for each alcohol used, showing both a homogenous and a phase separated area.

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ABSTRACT

Fast pyrolysis liquid or bio-oil has been used in engines with limited success. It requires a pilot fuel and/or an additive for successful combustion and there are problems with materials and liquid properties. It is immiscible with all conventional hydrocarbon fuels. Biodiesel, a product of esterification of vegetable oil with an alcohol, is widely used as a renewable liquid fuel as an additive to diesel at up to 20%. There are however limits to its use in conventional engines due to poor low temperature performance and variability in quality from a variety of vegetable oil qualities and variety of esterification processes. Within the European Project Bioliquids-CHP – a joint project between the European Commission and Russia – a study was undertaken to develop small scale CHP units based on engines and microturbines fuelled with bioliquids from fast pyrolysis and methyl esters of vegetable oil. Blends of bio-oil and biodiesel were evaluated and tested to overcome some of the disadvantages of using either fuel by itself. An alcohol was used as the co-solvent in the form of ethanol, 1-butanol or 2-propanol. Visual inspection of the blend homogeneity after 48 h was used as an indicator of the product stability and the results were plotted in a three phase chart for each alcohol used. An accelerated stability test was performed on selected samples in order to predict its long term stability. We concluded that the type and quantity of alcohol is critical for the blend formation and stability. Using 1-butanol gave the widest selection of stable blends, followed by blends with 2-propanol and finally ethanol, thus 1-butanol blends accepted the largest proportion of bio-oil in the mixture.

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1. Introduction

Interest in bioliquids as fuels derived from biomass has grown recently due to a number of reasons, but mainly for their positive effect in reducing carbon emissions. The term bioliquid, defines as a liquid fuel for energy purposes other than for transport, including electricity and heating and cooling, produced from biomass [1] includes, among others, fast pyrolysis oil (bio-oil), intermediate and slow pyrolysis heavy oil fraction after phase separation, vegetable and animal derived oil, used cooking oil, and transesterified vegetable and animal oil (biodiesel). Bioliquids are used mainly for small scale power and heat generation, however, commercial use of fast pyrolysis oils is very limited. The main advantages of bioliquids when compared to raw (solid) biomass are its higher energy density and availability on demand, thus it is easier for bioliquids to be stored and transported.

Pure vegetable oil and biodiesel are intended to be used in specific and distinctive markets: while both are used in stationary heat and power applications, biodiesel is also seen as an alternative transportation fuel. The composition of blends of diesel and biodiesel are defined by the “B” prefix, where B100 is 100% biodiesel, and thus B5 refers to a blend of 5 vol.% biodiesel and 95 vol.% conventional petro diesel. The latter is currently widely used in the European transportation market. In a fast pyrolysis process, biomass decomposes to generate mainly vapours that, after cooling and condensing, result in a dark liquid referred to as bio-oil with a lower heating value about 40% of conventional diesel. The liquid can be stored, used for energy generation, upgraded to biofuels or used for chemicals [2].

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Blending together bioliquids could widen their field of applications as an alternative green fuel. A blend could allow for mixtures to be created with improved properties to enable matching of the blend to the requirements of the application, such as a desired viscosity or a target minimum heating value, therefore the main advantage of blending bioliquids is the prospect of greater synergies and wider applications. This is especially important when considering this new fuel could be made 100% from renewable sources, therefore maximising the already known benefits of a renewable chain.

Bio-oils are known to be immiscible with biodiesel, generally forming an unstable mixture that breaks (phase separates) after a short period of time. This paper will show the results obtained when mixing bio-oil, biodiesel with an alcohol. It has been found that the polar properties of alcohols allow blends of bio-oil and biodiesel to become macroscopically stable over long periods of time. This paper will show that stable blends between bio-oil, biodiesel and alcohols are not only feasible, but also remain as a homogeneous single phase stable liquid with time. A series of tests that vary the proportion of each of the three components with different alcohols was used to build a three phase diagram to identify the boundary between miscibility and non-miscibility. Properties were either calculated or measured, with special attention to the visual observation of the miscibility of the blends.

2. Objectives

This study considers the miscibility of bio-oil and biodiesel in the presence of bio-derived alcohols. The main objective of this study is to prepare blends of bio-oil, biodiesel and bio-alcohols in order to assess their macroscopic visual homogeneity. The results were used for build a three phase diagram depicting the blend stability and identifying regions of miscibility and non-miscibility. The role of the various bio-derived alcohols as co-solvent in the blend is evaluated in the form of the weight proportion required to make a stable blend. Ideally the alcohol content should be minimised but in reality this should not compromise the homogeneity of the blend.

The “ageing” process in fast pyrolysis oil is well documented [3]. Because of ageing and miscibility issues, the blend stability is of vital importance. As there is no universally accepted standard for testing the blend stability with time, an accelerated test following the procedure established by Oasmaa et al. [4] was performed on a limited number of samples in the expectation this methodology can be used as a predictive tool in order to establish the blend robustness.

Table 1
Pyrolysis types and yields.

Type	Temp. (°C)	Residence time (s)	Yield: liquid/solid char/gas (wt.%)
Fast pyrolysis	500	1–2	75/12/13
Intermediate pyrolysis	500	5–20	50 (in two phases)/25/25
Slow pyrolysis	400	Hours to days	30/35/35
Gasification	750–900	1–2	5/10/85
Torrefaction	290	600–3600	Up to 10 if condensed/80 solid/20

3. Components properties

3.1. Bio-oil

Pyrolysis is a well-known process in which the chemical decomposition of natural materials takes place within a heated environment in the absence of oxygen. During pyrolysis, organic materials are transformed into a gaseous combustible fraction, a liquid fraction and a solid residue which includes fixed carbon and ash. The off-gases are cooled and condensed producing an oil/tar residue. There are three types of pyrolysis process depending on the particle residence time and operating reactor temperature [5], as shown in Table 1.

The bio-oil used in this study was manufactured by the Biomass Technology Group (BTG) in the Netherlands and is derived from softwood (pine). It is a dark brown free flowing liquid with a smoky smell. The molecular weight of the components varies considerably between samples, due to the differences between feedstock or biomass resource used. Bio-oil is constituted from many hundreds of oxygenated organic compounds in an aqueous substrate, with water as the largest single component. As well as the biomass resource used, the feedstock preparation and the pyrolysis process conditions also have an influence on the bio-oil properties. In addition, different pyrolysis reactor designs will also give different bio-oil characteristics. Bio-oil is different from other fuels in terms of chemical composition and properties, as shown in Table 2.

3.2. Biodiesel

Biodiesel is produced through the transesterification of vegetable oils with short-chain alcohols typically methanol, in order to yield fatty acid methyl esters (FAMEs) and glycerol [6]. It is a sulphur free, biodegradable, clear amber–yellow liquid with a iscosity similar to diesel. Typical diesel [7] and biodiesel [8] properties are shown in Table 2. Current diesel available at UK filling stations is a mixture of 95% conventional petro diesel and 5% biodiesel. Blends are named after the biodiesel proportion in the mixture, thus B10 is a 10% biodiesel and 90% petro diesel blend. The heating value of biodiesel used in transportation fuels is about 38 MJ/kg (LHV), slightly lower than conventional diesel. Biodiesel properties from different sources are

Table 2
Typical bio-oil properties range.

Property	Pyrolysis oil	Biodiesel	Diesel	
Moisture content	wt.%	25%	0.05% (vol)	161 ppm by wt
pH		2.5		
Specific gravity	kg/dm^3	1.20	0.88	0.85
Elemental analysis				
C	wt.%	56%	77%	87%
H	wt.%	6%	12%	13%
O	wt.%	38%	11%	0
N	wt.%	0 to 0.1%		
HHV as produced	MJ/kg	17	37.95 (LHV)	44.9
Viscosity	cSt (40 °C)	30–85 (25% water)	4.0–6.0	2.60
Solids (Char)	wt.%	0.1%		
Vacuum distillation residue		Up to 50%		

Table 3
Biodiesel properties from different sources.

	Palm oil	Sunflower oil	Tallow	Diesel	B20 diesel	Waste frying palm zoil
Kinematic viscosity (cSt)	5.7	4.6	–	3.06	3.2	6.32
Cetane No.	62.0	49	–	50	51	62
Low heating value (MJ/kg)	33.5	33.5	–	43.8	43.2	39.87
Cloud point (°C)	13.0	1	12	–	–	–
Pour point (°C)	–	–	9	−16	−16	10
Flash point (°C)	164.0	183	96	76	128	130
Density (kg/m^3)	880.0	860	–	855	859	877.2

Table 4
Typical alcohol properties.

Property (units)	Ethanol	1-Butanol	2-propanol
Molecular weight	46.1	74.1	60.1
Density (kg/m^3)	785.0	806	800
Boiling temperature (°C)	258.3	117.7	97.2
Flash point (°C)	8	30	15
Refractive index	1.359	1.397	1.384

Table 5
Blends proportions.

Bio-oil (%)	Biodiesel (%)	Alcohol (%)
10	10	80
20	20	60
30	30	40
40	40	20
10	40	50
20	30	50
30	20	50
40	10	50

Table 6
Blends for the three phase diagram organised by alcohol (wt.% bio-oil, biodiesel, alcohol).

Ethanol series	1-Butanol series	2-Propanol series
03 (10,10,80) ethanol	04 (10,10,80) 1-butanol	05 (10,10,80) 2-propanol
06 (20,20,60) ethanol	07 (20,20,60) 1-butanol	08 (20,20,60) 2-propanol
09 (30,30,40) ethanol	10 (30,30,40) 1-butanol	11 (30,30,40) 2-propanol
12 (40,40,20) ethanol	13 (40,40,20) 1-butanol	14 (40,40,20) 2-propanol
15 (10,40,50) ethanol	16 (10,40,50) 1-butanol	17 (10,40,50) 2-propanol
18 (20,30,50) ethanol	19 (20,30,50) 1-butanol	20 (20,30,50) 2-propanol
21 (30,20,50) ethanol	22 (30,20,50) 1-butanol	23 (30,20,50) 2-propanol
24 (40,10,50) ethanol	25 (40,10,50) 1-butanol	26 (40,10,50) 2-propanol

compared to diesel, commercial blend B20 [9] and waste frying palm oil [10] in Table 3.

It has been reported that biodiesel can improve the lubrication properties of diesel in the blend due to the presence of the methyl ester, thus biodiesels could reduce long term engine wear in internal combustion engines especially with very low sulphur diesel where lubrication is a problem. It appreciably reduces smoke and CO emissions when used pure (B100) as a direct fuel replacement [11]. However, tests employing pure biodiesel in internal combustion engines show distinctive problems associated with its combustion, mainly due to the inherent variability of the biodiesel source. In addition, pure biodiesel has poor low temperature behaviour, thus having a negative impact on the engine performance and reliability. The biodiesel used in this study is derived from used cooking oil and was bought from Sunflower Fuels in Devon, UK.

3.3. Alcohols

The alcohols used for the preparation of blends for this study are commercial stock bought from Fisher Scientific. Both ethanol and butanol are significant as they can be produced from biomass by fermentation, thus maintaining close to 100% renewability. Some of the chemical and physical properties for ethanol, 1-butanol and 2-propanol are shown in Table 4 [12].

4. Blends

4.1. Biodiesel and pyrolysis oil

Blends of biodiesel and slow pyrolysis oil obtained from pine chips at atmospheric pressure conditions have been tested in the past [13]. These blends were prepared after the separation of the heavy organic phase. Both the heavy organic bottom phase and the aqueous top phase were used for blending with biodiesel. The blends of organic phase with biodiesel and aqueous phase with biodiesel were allowed to phase separate and were characterised. Although the resulting mixtures were reported as feasible with only minor changes in the biodiesel properties such as increases in density and viscosity of the blend, a change in the blend heating value and solid residue was also noted. The blends for this particular study were prepared at 60 °C and left to cool at 25 °C, which the authors claim could have had a significant impact on the blend stability.

4.2. Bio-oil and ethanol blends

There has been limited experience in the preparation and testing of bio-oil and ethanol in internal combustion engines [14]. The study looked into the combustion of bio-oil produced via the fast pyrolysis of a spruce feedstock blended with ethanol.

Table 7
Blends for the three phase diagram fine tuning organised by alcohol (wt.% bio-oil, biodiesel, alcohol).

Ethanol series	1-Butanol series	2-Propanol series	Sample size (kg)
36 (20,10,70) ethanol	37 (20,10,70) 1-butanol	38 (20,10,70) 2-propanol	0.050
39 (25,15,60) ethanol	40 (25,15,60) 1-butanol	41 (25,15,60) 2-propanol	0.059
42 (27,18,55) ethanol	43 (27,18,55) 1-butanol	44 (27,18,55) 2-propanol	0.063
45 (10,30,60) ethanol	46 (10,30,60) 1-butanol	47 (10,30,60) 2-propanol	0.050
48 (14,34,52) ethanol	49 (14,34,52) 1-butanol	50 (14,34,52) 2-propanol	0.058
51 (17,35,48) ethanol	52 (17,35,48) 1-butanol	53 (17,35,48) 2-propanol	0.063
	54 (20,50,30) 1-butanol		0.020
	55 (40,30,30) 1-butanol		0.020
	56 (60,10,30) 1-butanol		0.020
	57 (60,20,20) 1-butanol		0.020
	58 (20,60,20) 1-butanol		0.020
	59 (25,38,37) 1-butanol		0.020
	60 (45,18,37) 1-butanol		0.020
	61 (55,35,10) 1-butanol		0.020

Table 8
Blend components heating value.

Component	Lower heating value (MJ/kg)
Bio-oil	17.0
Biodiesel	33.5
Ethanol	29.7
1-Butanol	33.1
2-Propanol	33.6

Table 9
Calculated blend low heating value (wt.% bio-oil, biodiesel, alcohol).

Sample identification	Heating value (MJ/kg)
3 (10,10,80) ethanol	28.81
4 (10,10,80) 1-butanol	31.93
5 (10,10,80) 2-propanol	31.51
6 (20,20,60) ethanol	27.92
7 (20,20,60) 1-butanol	30.26
8 (20,20,60) 2-propanol	29.95
9 (30,30,40) ethanol	27.03
10 (30,30,40) 1-butanol	28.59
11 (30,30,40) 2-propanol	28.38
12 (40,40,20) ethanol	26.14
13 (40,40,20) 1-butanol	26.92
14 (40,40,20) 2-propanol	26.82
15 (10,40,50) ethanol	29.95
16 (10,40,50) 1-butanol	31.90
17 (10,40,50) 2-propanol	31.64
18 (20,30,50) ethanol	28.30
19 (20,30,50) 1-butanol	30.25
20 (20,30,50) 2-propanol	29.99
21 (30,20,50) ethanol	26.65
22 (30,20,50) 1-butanol	28.60
23 (30,20,50) 2-propanol	28.34
24 (40,10,50) ethanol	25.00
25 (40,10,50) 1-butanol	26.95
26 (40,10,50) 2-propanol	26.69
36 (20,10,70) ethanol	27.54
37 (20,10,70) 1-butanol	30.27
38 (20,10,70) 2-propanol	29.90
39 (25,15,60) ethanol	27.10
40 (25,15,60) 1-butanol	29.44
41 (25,15,60) 2-propanol	29.12
42 (27,18,55) ethanol	26.96
43 (27,18,55) 1-butanol	29.10
44 (27,18,55) 2-propanol	28.81
45 (10,30,60) ethanol	29.57
46 (10,30,60) 1-butanol	31.91
47 (10,30,60) 2-propanol	31.60
48 (14,34,52) ethanol	29.21
49 (14,34,52) 1-butanol	31.24
50 (14,34,52) 2-propanol	30.97
51 (17,35,48) ethanol	28.87
52 (17,35,48) 1-butanol	30.74
53 (17,35,48) 2-propanol	30.49
54 (20,50,30) 1-butanol	30.07
55 (40,30,30) 1-butanol	26.77
56 (60,10,30) 1-butanol	23.47
57 (60,20,20) 1-butanol	23.52
58 (20,60,20) 1-butanol	30.12
59 (25,38,37) 1-butanol	29.22
60 (45,18,37) 1-butanol	25.92
61 (55,35,10) 1-butanol	24.38

Three stable blends containing 10%, 20% and 40% bio-oil by weight were tested and the results showed that up to 20% bio-oil in ethanol has limited impact on the performance of combustion of ethanol alone, while 40% bio-oil in ethanol produced instability in the combustion process.

Table 10
Single phase blends pH as measured (wt.% bio-oil, biodiesel, alcohol).

Sample	pH
Biodiesel	9.08
Bio-oil	2.27
4 (10,10,80) 1-butanol	4.38
5 (10,10,80) 2-propanol	4.39
6 (20,20,60) ethanol	4.17
7 (20,20,60) 1-butanol	4.05
8 (20,20,60) 2-propanol	4.23
10 (30,30,40) 1-butanol	3.79
16 (10,40,50) 1-butanol	4.47
17 (10,40,50) 2-propanol	4.46
19 (20,30,50) 1-butanol	4.18
20 (20,30,50) 2-propanol	4.12
22 (30,20,50) 1-butanol	3.82
23 (30,20,50) 2-propanol	3.97
25 (40,10,50) 1-butanol	3.82
26 (40,10,50) 2-propanol	3.8
36 (20,10,70) ethanol	4.04
37 (20,10,70) 1-butanol	4.09
38 (20,10,70) 2-propanol	3.9
39 (25,15,60) ethanol	4.06
40 (25,15,60) 1-butanol	4.08
41 (25,15,60) 2-propanol	3.84
43 (27,18,55) 1-butanol	3.9
44 (27,18,55) 2-propanol	3.71
45 (10,30,60) ethanol	4.31
46 (10,30,60) 1-butanol	4.3
47 (10,30,60) 2-propanol	4.33
48 (14,34,52) ethanol	4.21
49 (14,34,52) 1-butanol	4.32
50 (14,34,52) 2-propanol	4.36
52 (17,35,48) 1-butanol	4.22
53 (17,35,48) 2-propanol	4.19
59 (25,38,37) 1-butanol	3.77
60 (45,18,37) 1-butanol	3.47

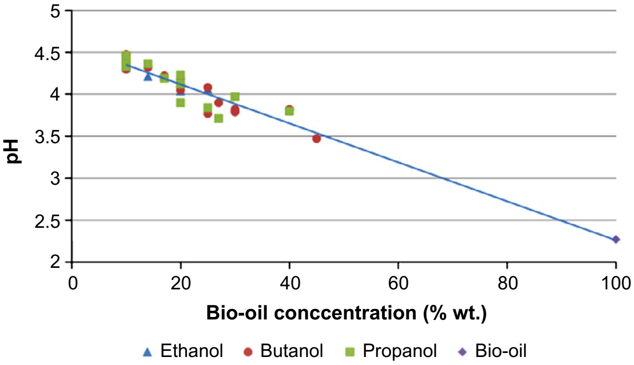

Fig. 1. Single phase blends pH as measured organised by alcohol.

Table 11
Blends water content, density and flash point as measured (wt.% bio-oil, biodiesel, alcohol).

Sample	Water content (wt.%)	Density (g/cm^3)	Flash point (°C)
Biodiesel	0.1	0.888	34
Diesel	161 ppm by wt	0.706	60–80
Bio-oil	22.83	1.224	<25
6 (20,20,60) ethanol	4.86	0.882	17
10 (30,30,40) 1-butanol	6.76	0.933	42
23 (30,20,50) 2-propanol	6.97	0.913	17
60 (45,18,37) 1-butanol	10.4	0.979	42

4.3. Other bio-oil upgrading techniques

Bio-oil has been the subject of extensive studies in the past in which the main objective is to upgrade the original product into a more stable and desirable fuel via physical, catalytic or chemical techniques [15]. Physical treatment includes filtration for removing the ash and alkali, solvent addition in order to reduce the bio-oil viscosity and improve the oil stability, and emulsification (5–30% bio-oil in diesel) for use as diesel miscible transportation fuels. Catalytic processing aims to produce an upgraded bio-oil with lower oxygen content and higher heating value via deoxygenation and conventional refining techniques. Hydrotreating and Zeolite cracking are the most studied processes; however, catalytic upgrading of bio-oil can also be integrated during the pyrolysis process for products compatible with refinery streams. Chemical treatment include aqueous phase processing, steam reforming and aqueous phase reforming for producing hydrogen and alkanes, mild cracking, and esterification for an improved bio-oil (reduced water, higher stability) without the need for full deoxygenation.

Table 12
Accelerated stability test results.

Test	Value before	Value after	Variation
10 (30,30,40) 1-butanol			
Weight (g)	250.65	250.52	−0.05%
Water content (wt.%)	7.38	7.64	0.03
Viscosity (cP)	4.98	4.88	−0.02
60 (45,18,37) 1-butanol			
Weight (g)	255.68	255.65	−0.01%
Water content (wt.%)	11.02	11.86	0.08
Viscosity (cP)	6.97	6.81	−0.02

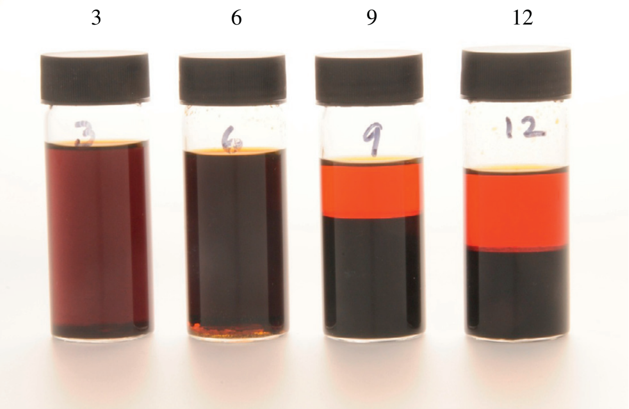

Fig. 2. First set of blends with ethanol.

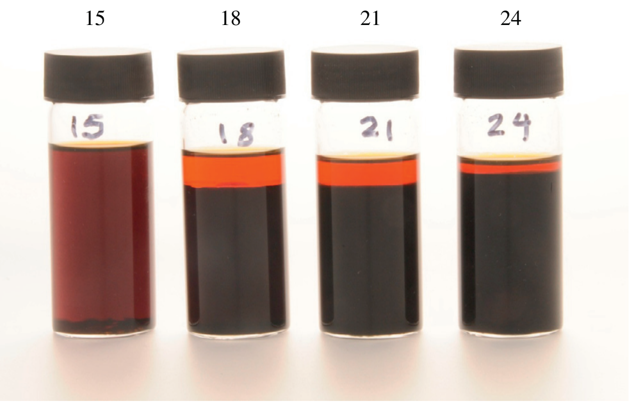

Fig. 3. Second set of blends with ethanol.

4.4. Bio-oil, biodiesel and alcohols blends

A number of steps were developed for the preparation of the blends samples and a series of test were carried out in order to establish their characteristics. In addition, some properties were calculated based on the components proportions.

4.4.1. Mixing methodology

The blends were prepared following a simple yet rigorous procedure: The bio-oil was weighted in the container first, followed by the biodiesel. The alcohol was then added and the container was sealed and lightly shaken. A photograph was taken 48 h later to document its appearance and the quality of the blend.

4.4.2. Sample labelling

The samples were labelled using a reference to its component proportions in the following layout:

Sample No. (*wt*.% *bio-oil*, *wt*.% *biodiesel*, *wt*.% *alcohol*) *alcohol*

Thus *20* (*20*,*30*,*50*) *2-propanol* represents sample No. 20 made out of 20 wt.% bio-oil, 30 wt.% biodiesel and 50 wt.% 2-propanol. The blend proportions were selected on the basis of covering a wide spectrum of feasible blends, with the objective of using the information for building a three-phase blending diagram. Table 5 has the generic blends proportions. All blends were prepared at 25 °C.

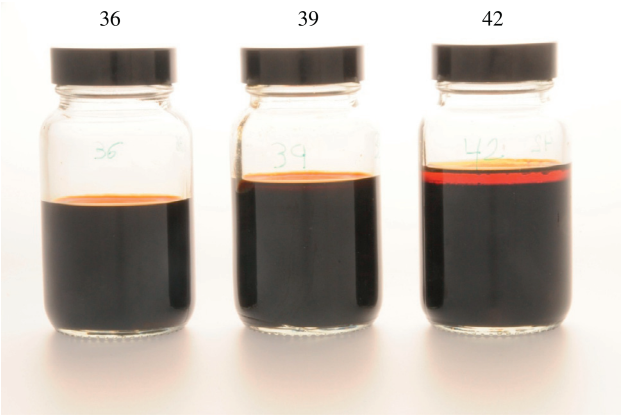

Fig. 4. Third set of blends with ethanol.

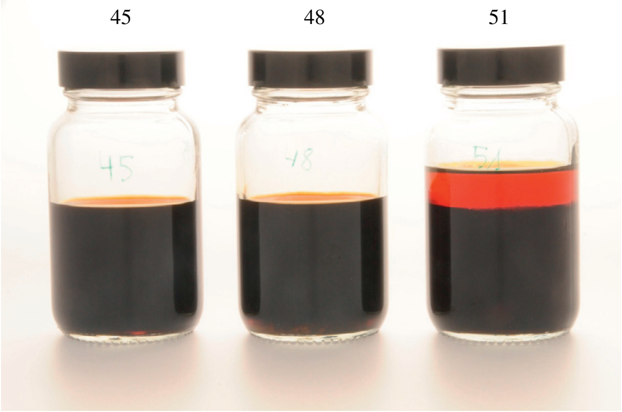

Fig. 5. Fourth set of blends with ethanol.

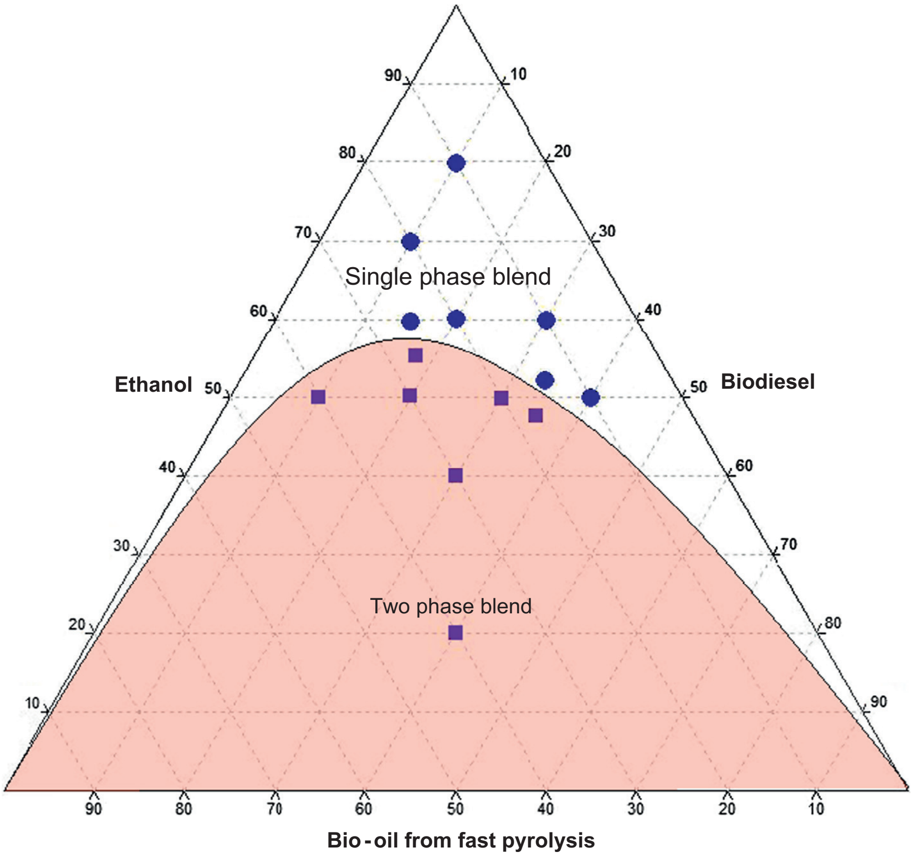

Fig. 6. Three phase diagram for ethanol blends.

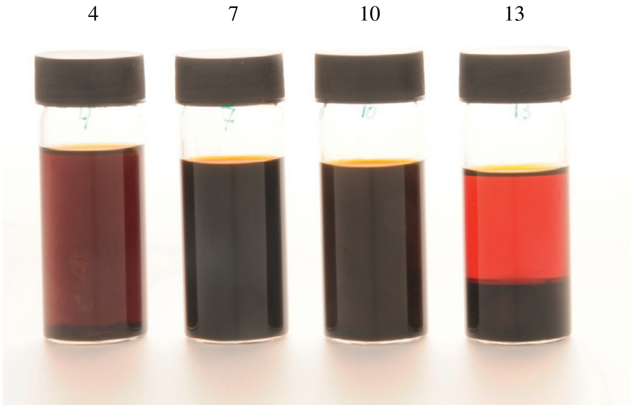

Fig. 7. First set of blends with 1-butanol.

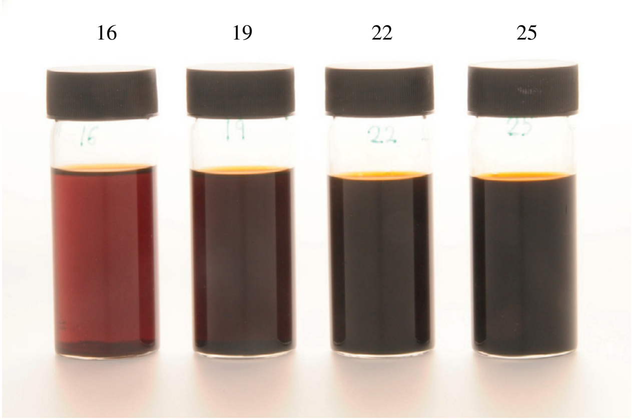

Fig. 8. Second set of blends with 1-butanol.

4.4.3. Three phase diagram samples

The blend sample size was fixed at 0.02 kg and prepared in clear glass containers. A list of samples is shown in Table 6 below:

4.4.4. Three phase diagram fine tuning samples

Previous experience suggested that the boundary between miscible and non-miscible blends needs careful definition and extra care, so additional samples were prepared as summarised in Table 7. Note that blends with 1-butanol were of special interest; therefore, a more detailed investigation was carried out for this particular alcohol.

5. Results

5.1. Low heating value

The blend lower heating value was calculated from the component proportions in the blend using the weighted average equation. In Table 8 the individual components lower heating value is shown.

A summary of the calculated lower heating values is shown in Table 9.

It was expected that all blends would show an increased heating value when compared to the original fast pyrolysis oil. The increase can be tailored to the user needs, in a compromise between the blend stability, viscosity and water content, but in all cases must be homogenous and stable.

5.2. pH results

A summary of the measured pH values for selected one phase blends is presented in Table 10 and Fig. 1.

The trend is clear: the pH will be lower as the proportion of bio-oil concentration increases.

5.3. Water content, density and flash point results

The water content, density and flash point were measured for selected samples. Water content was measured in-house, while density and flash point were sent to an external laboratory. The results are shown in Table 11.

As expected, the blends have much lower water content when compared to the original fast pyrolysis oil. At the same time the density of the blends has decreased. In terms of the flash point, most reports suggest that flash point measurement is very difficult for bio-oil and that results, when obtained, are variable. The value of <25 °C reported in Table 11 was surprising. The flash point of the biodiesel from used cooking oil was also surprisingly low at 34 °C as reported by the independent laboratory, when typical values are around 100–170 °C [7].

5.4. Accelerated stability results

There is no accepted standard procedure for estimating the long term stability of fast pyrolysis oil, although there is a methodology that has been used in the past [3]. The methodology was reviewed and adopted for fast pyrolysis oil/biodiesel/alcohols blends. The procedure involves measuring viscosity and/or water content before and after the sample is subjected to a 24 h continuous heating at 80 °C [4]. This is believed to reliably mimic the stability over 12 months at ambient temperature. The variation in a particular property is calculated using the equation below:

$$\Delta\ property = (X_2 - X_1)/X_1$$

where *Δ property* is the property variation; X_2 is the property measured after the heating process (water content or viscosity) and X_1 is the property measured before the heating process (water content or viscosity).

The properties to measure can be either water content or viscosity. The sample weight is also recorded in order to make sure no evaporation took place during the test. In Table 12 the results for selected blends is shown:

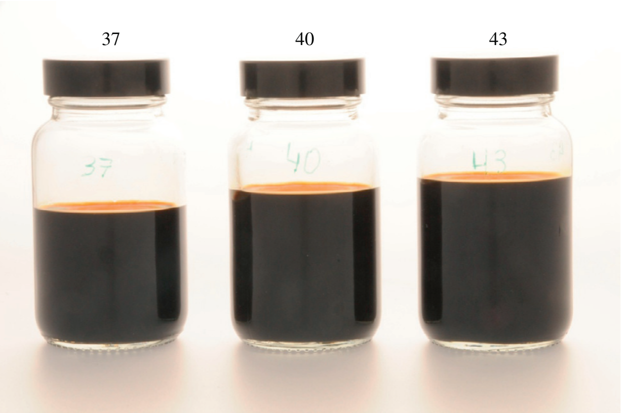

Fig. 9. Third set of blends with 1-butanol.

The weight loss is less than 0.1% for these samples. As the variations in both water content and viscosity are small, the stability of the blends can be described as remarkably good, especially when compared to fast pyrolysis oils [4]. The blend is expected to remain unaltered for up to 1 year while in storage.

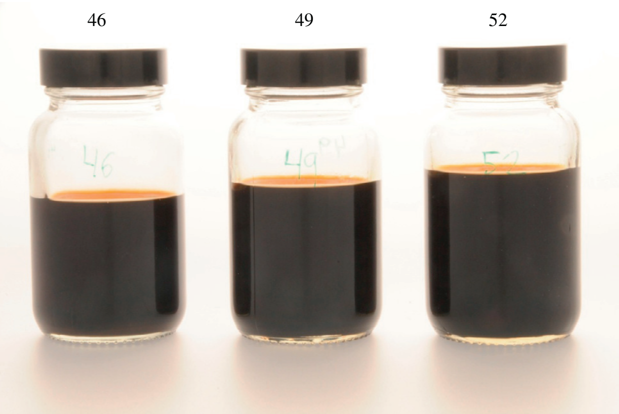

Fig. 10. Fourth set of blends with 1-butanol.

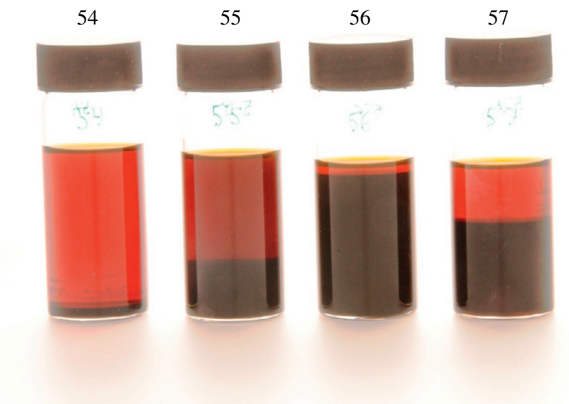

Fig. 11. Fifth set of blends with 1-butanol.

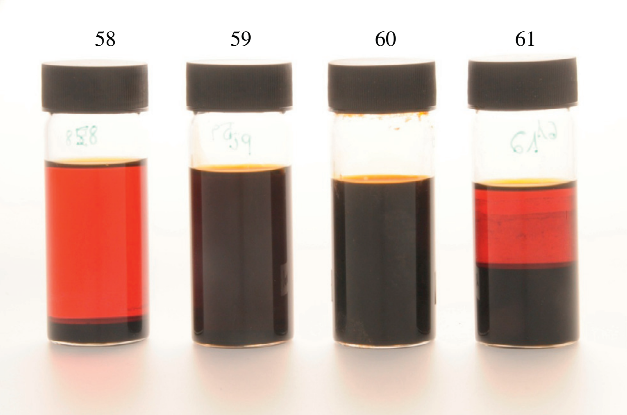

Fig. 12. Sixth set of blends with 1-butanol.

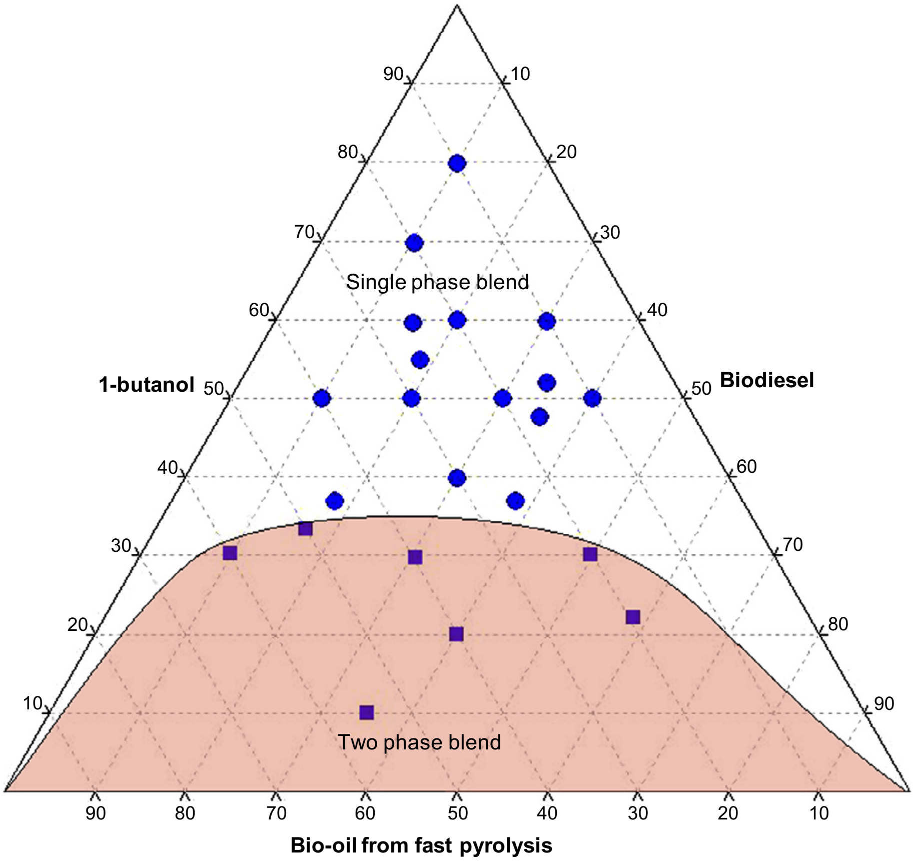

Fig. 13. Three phase diagram for 1-butanol blends.

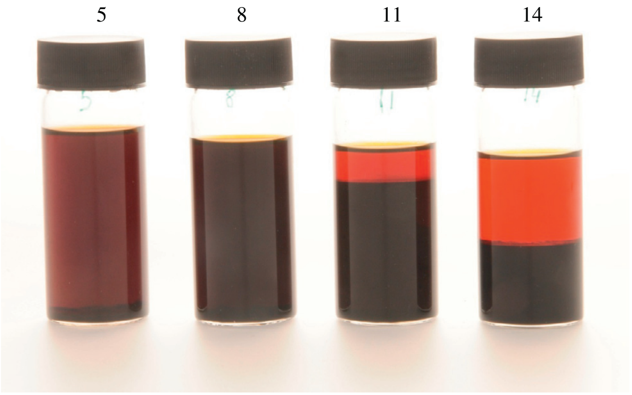

Fig. 14. First set of blends with 2-propanol.

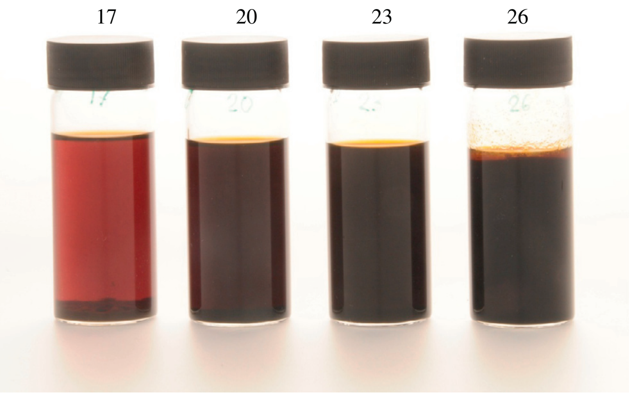

Fig. 15. Second set of blends with 2-propanol.

5.5. Photography

A photograph was taken of every sample in order to document its appearance. The picture was taken using a white background with a strong backlight in order to enhance the picture and distinguish the phase boundary if present. The results of the photographic evidence were used to build the three-phase diagrams.

5.5.1. Ethanol samples

Photographic evidence of the blends made with ethanol is shown next.

Fig. 2 gives evidence of phase separation for samples No. 9 (30,30,40) and No. 12 (40,40,20), while samples No. 3 (10,10,80) and No. 6 (20,20,60) are homogeneous.

Similar to the previous picture, Fig. 3 shows that blends samples No. 18 (20,30,50); No. 21 (30,20,50) and No. 24 (40,10,50) are not homogeneous. Only sample No. 15 (10,40,50) is a single phase blend.

Fig. 4 shows that samples No. 36 (20,10,70) and No. 39(25,15,60) are homogeneous while sample No. 42 (27,18,55) has phase separated, suggesting the proportions are not well suited for their role. It may be that the alcohol as bonding agent is not present in sufficient quantity, it has not developed its role or the other components have surpassed their stable limit for this instance.

Fig. 5 shows that sample No. 51 (17,35,48) is not homogeneous while samples No. 45 (10,30,60) and No. 48 (14,34,52) are homogenous.

Using this information a three-phase diagram was constructed in Fig. 6 in which the proportion of each component is shown in the axes. A curve has been drawn along the proposed boundary between homogeneous samples and phase separated samples. Similarly, a three phase diagram was constructed for 2-propanol and 1-butanol.

5.5.2. 1-Butanol samples

The pictures shown for butanol blends (Figs. 7–11) were taken 48 h after preparation.

It can be seen that only sample No. 13 (40,40,20) is non-homogeneous.

All samples shown in Fig. 11 are non-homogeneous.

In Fig. 12 samples No. 59 (25,38,37) and No. 60 (45,18,37) are homogeneous. The resultant three-phase diagram is shown in Fig. 13 with a suggested phase change boundary.

5.5.3. 2-Propanol samples

Figs. 14–17 show the resulting blends when using 2-propanol after standing for 48 h.

Fig. 14 reveals that both sample No. 11 (30,30,40) and sample No. 14 (40,40,20) are not homogeneous.

Figs. 15 and 16 show homogenous blends. With the exception of sample No. 11 and sample No. 14, all 2-propanol blends remained homogeneous. The proposed three-phase diagram is shown in Fig. 18.

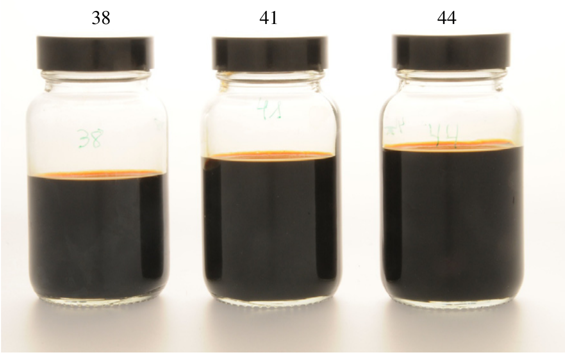

Fig. 16. Third set of blends with 2-propanol.

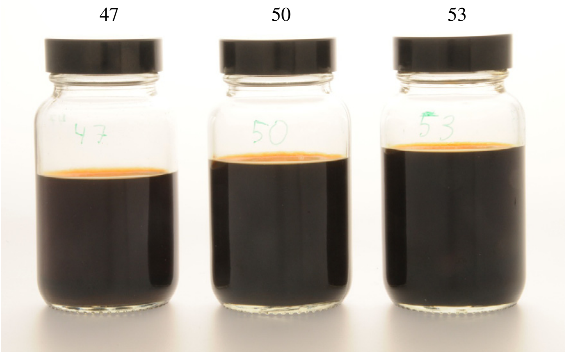

Fig. 17. Fourth set of blends with 2-propanol.

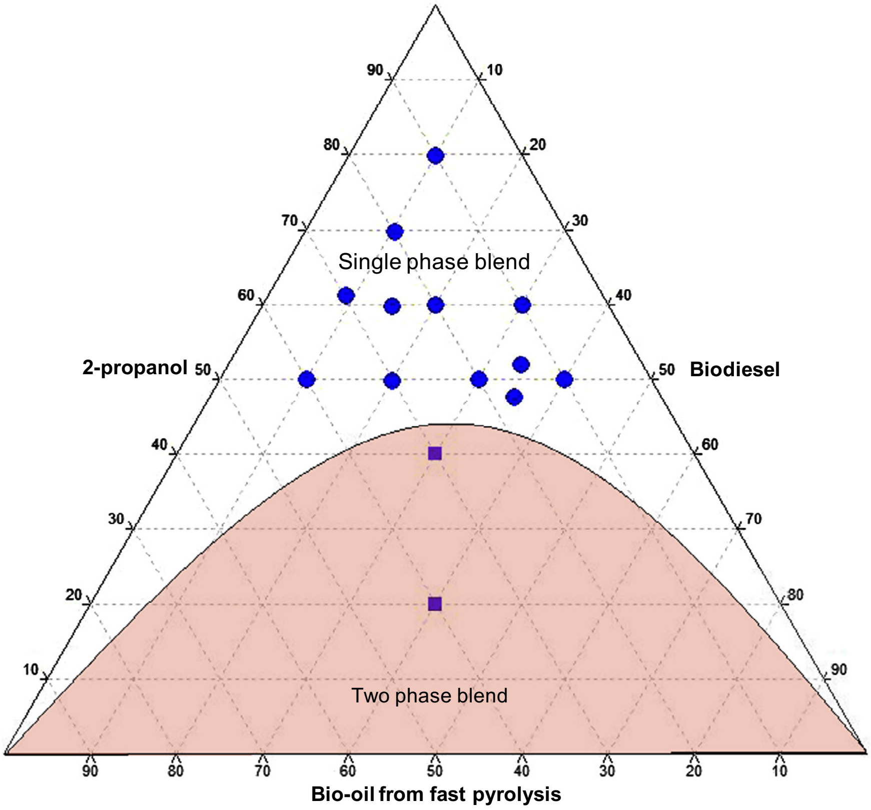

Fig. 18. Three phase diagram for 2-propanol blends.

6. Conclusions

It is possible to prepare homogenous blends of bio-oil and biodiesel in the presence of an alcohol that are extremely stable over time, particularly in comparison with bio-oil. These blends are an attractive option for combined heat and power production as the resultant viscosity is much lower when compared to other bio-oil upgrading techniques.

The miscibility of blends of bio-oil and biodiesel depends on the type and amount of alcohol employed. Therefore, by selecting the appropriate alcohol and proportions of components, a tailor-made blend can be made to suit the user requirements.

Both 1-butanol and 2-propanol produced homogenous blends over a wider range of bio-oil contents compared to ethanol.

Relative to the alcohol in the blend, we can conclude that:

- A blend containing 50% ethanol is likely to be border-line in terms of stability. However, the presence of more than 50% ethanol is a good indicator that the resulting blend will be homogeneous.
- A blend containing less than 30% 1-butanol is likely to be phase separated.
- A blend containing less than 40% 2-propanol is likely to be phase separated.
- 1-Butanol based blends can tolerate a maximum of 60 wt.% bio-oil.
- 2-Propanol based blends can tolerate a maximum of 50 wt.% bio-oil.
- Ethanol based blends can tolerate a maximum of 35 wt.% bio-oil.

The accelerated stability test showed negligible changes in water content and viscosity for the selected butanol blends. It is therefore expected that they will remain stable and homogeneous after 1 year in storage.

The effect of the use of an alcohol in reducing the viscosity and water content is a great advantage from the handling point of view, and the results from the accelerated stability test are particularly encouraging. Low pH continues to represent a challenge but is a consequence of the bio-oil concentration in the blend, thus the use of specialised materials is encouraged for direct contact with blends. The use of biodiesel further enhances the environmental credentials of the blends, as all the primary components can be related to sustainable sources. In summary, upgrading bio-oils by means of blending with biodiesel and alcohols represent a significant advantage over the use of bio-oil on its own, as the blend can be tailored for the specific application.

Acknowledgments

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